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INFORMATION REPORT

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COUNTRY USSR

SUBJECT Soviet Research on Synthesis and Insecticidal
Properties of Some Mixed Esters of Dithiophosphoric
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THIS IS UNEVALUATED INFORMATION

SOURCE

1. I have recently come across an article entitled "Synthesis of Some Mixed Esters of Dithiophosphoric Acid" by N N Mel'nikov and K D Shvetsova-Shilovskaya, appearing in Doklady Akad Nauk, SSSR, 86,543-6 (1952). This article lists the properties of an entire series of phosphorous compounds similar to Parathion, an insecticide toxic to humans and a cholinesterase inhibitor. The phosphorous compounds listed in this article are also most likely to be toxic to humans and cholinesterase inhibitors. Of course, no data are given in the article on this phase, and I would be quite surprised if data had been given. Indeed, there is a fair assumption which can be made that probably some data on these compounds would have been given in the article, provided the compounds were not toxic to humans.
2. In the insecticide business it is impossible to tell whether compounds possess toxicity without actually experimenting with them on mice, rabbits, etc. This is done on a basis of body weight in which the results are analyzed and applied to human weights.
3. This article is the latest in a series of articles [redacted] having to do with organophosphorous compounds similar to Parathion, beginning with an article published in 1950 by N N Mel'nikov, one of the co-authors of the current article, and two of his colleagues, Ya A Mandel'daum and P V Popov, entitled "Synthesis and Insecticidal Properties of Some Esters of Phosphoric Acid" [redacted]. The 1950 article is the first acknowledgment in the Soviet press of compounds related to Parathion.

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4. [REDACTED] the 1952 article by Mel'nikov and Shvetsova-Shilovskaya as follows:
- It was shown that $(RO)_2PS_2H$ add to unsatd compounds ($PhCH:CH_2$, $CH_2:CHCO_2Me$, $CH_2:CHCN$, $CH_2:CHOAc$, $CH_2:CHCHO$, esters of maleic acid, etc) yielding the mixed esters of dithiophosphoric acid; the reaction occurs in the cold in the presence of small amounts of solid KOH. For best results 1 mole of unsatd compound was treated with $(RO)_2PS_2H$ at such rate as to keep temp at 40-50°; after standing at room temp until reaction ceased (titration of free acid with 0.1 N NaOH) the products were distd. The following are reported: $(MeO)_2PS_2CH(CO_2Et)CH_2CO_2Et$, 50%, $b_{3.5}^{160-70^\circ}$, $n_D^{20} 1.4960$, $d_4^{20} 1.2076$; P,P-di-Et analog, 59%, $b_{3.5}^{157-62^\circ}$, 1.4910, 1.1742; P,P-di-Pr analog, 27%, $b_{0.1}^{145^\circ}$, 1.4880, 1.1706; P,P di-iso-Pr analog 39%, $b_{4.151^\circ}$, 1.5440, 1.0702; P,P di-Bu analog, 40%, $b_{0.025}^{125-8^\circ}$, 1.4861, 1.1078; P,P di-iso-Bu analog, 15%, $b_{0.04}^{117-30^\circ}$, 1.4855, 1.0642; $(EtO)_2PS_2CH_2CH_2CN$, 33%, $b_{3.5}^{137-42^\circ}$, 1.5195, 1.1704; P,P di-Pr analog, 30%, $b_{0.05}^{116-20^\circ}$, 1.5068, 1.0505; P,P-di-Bu analog, 27.5%, $b_{0.03}^{121-3^\circ}$, 1.5050, 1.0816; P,P di-iso-Bu analog, 44%, $b_{0.05}^{122-3^\circ}$, 1.5010, 1.0986; $(MeO)_2PS_2CH_2CH_2O_2CMe$, 38%, $b_{2.100-3^\circ}$, 1.5252, 1.1558; P,P di-Et analog, 71%, $b_{1.5}^{115-17^\circ}$, 1.4948, 1.1517; P,P di-Pr analog, 46%, $b_{0.05}^{80-1^\circ}$, 1.5075, 1.0984; P,P di-iso-Pr analog, 50%, $b_{0.1}^{72-4^\circ}$, 1.4335, 1.846 (1.0846-?); P,P di-iso-Bu analog, 43%, $b_{0.075}^{104^\circ}$, 1.4858, 1.0926; P,P di-Bu analog, 25%, $b_{0.4}^{109^\circ}$, 1.4915, 1.0915; $(MeO)_2PS_2CHMePh$ (presumably) 50%, $b_{0.45}^{128-32^\circ}$, 1.5705, 1.2108; P,P di-Et analog, 35%, $b_{0.15}^{135-7^\circ}$, 1.5498, 1.1444; P,P di-Pr analog, 38.5%, $b_{0.1}^{129-31^\circ}$, 1.5381, 1.0990; P,P di-iso-Pr analog, 38.5%, $b_{0.2}^{121-4^\circ}$, 1.5365, 1.0966; P,P di-Bu analog, 13%, $b_{0.025}^{137-40^\circ}$, 1.5320, 1.0890; P,P di-iso-Bu analog, 17.5%, $b_{0.04}^{117-22^\circ}$, 1.5301, 1.0860; $(MeO)_2PS_2CH_2CH_2CO_2Me$, 67%, $b_{3.145^\circ}$, 1.5160, 1.2625; P,P di-Et analog, 83%, $b_{1.5}^{167^\circ}$, 1.5050, 1.1911; P,P di-iso-Bu analog, 58%, $b_{0.2}^{124-9^\circ}$, 1.4915, 1.1162; $(MeO)_2PS_2CH_2CH_2CHMeCO_2Me$ (presumably), 38%, $b_{2.133-5^\circ}$, 1.5100, 1.2330; P,P di-Et analog, 59%, $b_{5.154-5^\circ}$, 1.4995, 1.1577; P,P di-iso-Pr analog, 47%, $b_{0.02}^{84-5^\circ}$, 1.4935, 1.1203; P,P di-iso-Bu analog 56%, $b_{0.04}^{115-16^\circ}$, 1.4915, 1.1138; P,P di-Bu analog, 38%, $b_{0.025}^{110^\circ}$, 1.4918, 1.1132; adduct of $(iso-Pro)_2PS_2H$ and $CH_2:CHCHO$, 37%, $b_{0.15}^{74^\circ}$, 1.5040, 1.1348. It is stated that $(BuO)_2PS_2CH_2CH_2O_2CMe$ lost CO_2 during distn and the analytical data are given for the "decarboxylated ester".

5. It is not clear whether or not the constants cited are for the decarboxylated material.

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